

Third Quarterly Progress Report
1 January 1968 — 31 March 1968

**SILVER-ZINC BATTERY SEPARATOR
MATERIAL DEVELOPMENT**

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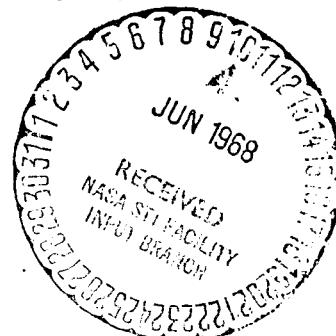
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ABSTRACT

Membranes for use as silver-zinc battery separators are being made of a copolymer of ethylene and acrylic acid which is formed by hydrolysis of vulcanized copolymer film of ethylene and methyl acrylate. Films made from copolymer with different proportions of monomers are being evaluated and optimum methods of vulcanizing, forming film and hydrolysis are being determined.

The degree of vulcanization has been found to be a critical variable and must be controlled by means of vulcanizing temperature, amount of vulcanizing agent and vulcanizing time. Under vulcanized membranes are unstable in caustic and over-vulcanized membranes have high resistance (incomplete hydrolysis probably).

Polyblending and carbon filling appear to be useful techniques for battery separators. By these methods, the tackiness of the precursor membranes may be reduced with subsequent easier handling. Additional benefits may also result but have not been defined as yet.

Sterilization at 140°C for 60 hours (40% KOH) has generally caused a small increase in the resistance of the membranes. However, the increase is small and the specific resistance of several membranes has been less than 10 ohm-in. before and after sterilization. The better membranes contain about 40% acrylic acid or more, copolymerized with ethylene.

Equipment is being assembled for the production of 100 feet of film. A 20 in. x 20 in. hydraulic press will be used to form film between Teflon sheets of copolymer blended on a roll mill with the vulcanizing agent. The vulcanized membranes will be sandwiched between polyolefin dividers and hydrolyzed in a steel kettle.

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1. OBJECTIVE

This project has been undertaken for the development and limited production of ethylene/acrylic acid (E/Acr A) membranes for use as separators in silver oxide-zinc batteries. The work includes the synthesis of ethylene/methyl acrylate copolymer (E/MAR), formation of film, vulcanization of the film and hydrolysis to E/Acr A. The copolymer film will be characterized, and 100 feet of the most acceptable product will be made.

2. SUMMARY AND CONCLUSIONS

Composites of E/20% MAR, E/30% MAR, E/40% MAR, E/50% MAR and E/60% MAR have been made by mixing on a heated roll mill the individual experimental samples. The monomer ratio of the individual samples was within 10% of the average of the composite. The composites have a relative uniform monomer distribution and are being used for film making and testing.

Uniform E/MAR film of predetermined thickness has been made by casting from toluene or benzene solution and vulcanizing in a separate step by ultraviolet irradiation. While this is the most satisfactory method for making 1 mil film, E/MAR of this thickness is tacky, rubbery and very difficult to handle. E/MAR about 3 mil thick is much easier to handle and seems to be more appropriate for this project. Three mil and thicker film may be formed in a hot press. In this method, the film is formed and vulcanized simultaneously. Fused E/MAR adheres strongly to all surfaces and the press plates must be covered with Teflon, from which 3 mil and thicker film may be removed without serious distortion.

The degree of vulcanization has been shown to be a governing factor in the preparation of suitable membranes. Vulcanization has been qualitatively evaluated by capillary extrusion rheometry. Membranes with little or no vulcanization disintegrate in the hydrolysis baths (2.5 N KOH), while membranes with excessive vulcanization do not hydrolyze readily; this results in a high resistance. Satisfactory membranes are vulcanized to a degree just exceeding the knot stage (E/MAR becomes insoluble in toluene at knot stage) and well short of the flake stage (E/MAR becomes infusible at flake stage).

Hydrolysis is a two-stage process. In the first stage, membranes are soaked for 24 hours in 2.5 N alcoholic KOH at 60-70°C. The second stage is similar: soaking in 2.5 N aqueous KOH. For hydrolysis of numerous large pieces (larger than 2 in. x 2 in.) of film, the individual films are separated with a porous polyolefin divider.

The properties of E/MAR and E/Acr A may be modified by blending them with other materials before forming the film. Polyblends of two or more E/MAR samples of widely differing monomer ratios and E/MAR with an ethylene/vinyl acetate (E/VA) copolymer are less tacky (and easier to handle) than a more homogeneous sample of E/MAR of comparable composition. A blend of E/MAR with 25% (by weight) carbon black is not tacky and appears interesting. In this blend, the carbon does not appear to contribute to conductance.

Membranes of E/Acr A have been tested for stability during sterilization at 140°C in 40% KOH for 60 hours. Membranes with adequate vulcanization appear to be quite stable. The AC resistance increased somewhat for several of the membranes but is still well below 20 ohm-in. specific resistance. The amount of increase of resistance may also be somewhat dependent on vulcanization.

Data for E/Acr A film made from E/20% MAR, E/30% MAR, E/40% MAR, E/50% MAR and E/60% MAR will be gathered shortly in order to determine the composition of the 100 feet of product for this project.

3. EXPERIMENTAL WORK

3.1 Copolymer Synthesis

A little time has been spent this quarter on synthesis of the precursor copolymer for conversion to battery separator film. A number of small samples of ethylene/methyl acrylate (E/MAR) have been made previously, and while the average monomer ratio has been controlled, no two samples are exactly alike. Therefore, several samples of copolymer have been blended together to give composites of E/20% MAR, E/30% MAR, E/40% MAR, E/50% MAR and E/60% MAR. The latter two composites are short supply and additional polymerizations will be necessary. The spread of composition in each composite was over a range of about 10%. These composites have been used and will be used for preparation of ethylene/acrylic acid (E/Acr A) film for test purposes.

3.2 Film Preparation

Two methods of forming E/MAR film prior to or concurrently with vulcanization have been evaluated: casting from solutions, and hot pressing. Extrusion, either blow extrusion or T-die extrusion, is an excellent method of forming thin films which should be considered for the preparation of sizable quantities of film. However, extrusion requires larger quantities of polymers than are now available and should be considered at a later date.

Film casting of E/MAR dissolved in toluene or benzene has produced thin films that are quite uniform in thickness. A solution with about 10 wt% E/MAR is made by warming and stirring (solution gels at room temperature). A Gardner knife has been used to spread the warm and somewhat viscous solution evenly onto a casting plate with a smooth surface. Both glass and ferro-type plates have been used for film casting. The solvent has been evaporated naturally or at slightly elevated temperature caused by a heat lamp. However, the films cannot be heated to around 100°C or higher since this causes the films to fuse and stick to the plates. When essentially free of solvent, the films are removed from the plates. Separation of the films is facilitated by moisture. The films prepared in this way, about 1.0 mil thick, are uniform and relatively free of defects.

Thicker or thinner films may also be made. However, 1 mil film of E/MAR is tacky, rubbery and difficult to handle. Tackiness increases with MAR content of the polymer. Vulcanization (in a separate step) improves this handling problem somewhat. E/MAR film about 3-5 mils thick is much easier to handle and less tacky. Therefore, we suggest that the product of this project (100 feet of film) be more than 1 mil thick and less than 5 mil thick.

Film has also been made by pressing polymer at a temperature above the softening temperature of the polymer in a machine press with heated platens. This process differs from that above in that vulcanization occurs simultaneously with film forming. The platens have been recently leveled but film generally varies by 1 mil in thickness. Therefore, 3-4 mil film is the preferred product, rather than 1 mil film. The press used for many of the films was obtained from the Pasadena Machine Company, has 12 in. x 12 in. platens and a ram force up to 30 ton.

The first films made in a hot press were made between stainless steel plates or aluminum foil. The film product was fused to the metal plates or foil and was very difficult to separate, causing distortion or tearing the film. Several mold release agents have been employed without appreciable success. The mold surfaces have been coated with polyvinyl alcohol which improved the film release slightly. A commercial fluorinated solvent (Du Pont "Slip-Spray") was applied to the mold surfaces without significant benefit. Coating the plates with cellophane was not particularly helpful, and the cellophane yellowed and decomposed during the heating. Teflon between the plates and the polymer has been used successfully to prepare pressed film. The polymer is placed between Teflon sheets about 5-10 mils thick and pressed between the platens. The pressure is increased gradually so that the Teflon sheets do not wrinkle. The film product still sticks to the Teflon sheets, but the adhesion is less than with other surfaces. Film may generally be pulled loose from the Teflon without serious distortion. E/MAR with 40% MAR or less is easier to handle than E/50% MAR and E/60% MAR. All proportions have been made and we suggest 3-5 mil film may be more satisfactory.

3.3 Vulcanization And Extrusion Rheometry

E/MAR film which is not vulcanized or crosslinked will disintegrate in strong caustic solutions such as those used in silver-zinc batteries. Vulcanizing the polymer makes stable film. However, early in this work, some vulcanized film, after hydrolysis to E/Acr A, had excessive AC resistance which seemed to result from excessive vulcanization, i.e., over-vulcanization. The effect may be caused by incomplete hydrolysis

of over-vulcanized polymer film or by decreased ion mobility through it. Therefore, the degree of vulcanization must be controlled. A method for qualitatively measuring vulcanization has been described by one of us [Salyer, et. al., J. Polym. Sci A 3, 1911 (1965)], and capillary extrusion rheometry has been employed in this project.

The degree of vulcanization is a function of time, temperature, and amount of vulcanizing agent present. E/MAR polymer is conveniently vulcanized at 150°C. DiCup R (dicumyl peroxide, recrystallized), which has a half life of about 12-15 seconds at this temperature (Wallace and Tiernan Brochure 30.30), has been used as the vulcanizing agent. For evaluation, a blend of the polymer and DiCup R is made on a roll mill at moderate temperature (100°C maximum) so that little or no vulcanization occurs. Some of the product is put in a melt index machine and extruded at a constant rate (melt index machine is Instron Tester) over a period of time at 150°C. The first extrudate is lightly vulcanized and flows smoothly. However, with time in the machine at 150°C, vulcanization continues and changes occur. At the knot time the extrudate becomes knotty and later the extrudate becomes flaky. The knot and flake times are indicative of degree of vulcanization, or, at constant temperature, a function of amount of vulcanizing agent. Rheometry data is shown in Table 1.

Table 1

VULCANIZATION - KNOT TIME

Temperature 150°C
 Instron Crosshead Travel 0.1 in/min.
 Orifice 0.043"
 Orifice L/D 15

<u>Sample</u>	<u>Copolymer Composition¹</u>	<u>DiCup R Wt%²</u>	<u>Knot Time-Min.³</u>	<u>Flake Time (min.)⁴</u>
82877-1	E/30% EAR	2.5	9	29
82877-3	E/30% EAR	7.5	<5	<5
82877-4	E/30% EAR	2.2	9	18
82877-6	E/30% EAR	6.6	5.5	10
87665-A	E/41.3% MAR	3.0	12	27
87665-B	E/41.3% MAR	10.0	5	9
87675-1	E/18.7% MAR	3.0	10	30
87675-2	E/18.7% MAR	10.0	<5	5
87680-A	E/60% MAR	3.0	9	22
87695-1	E/13.5% EAR	1.0	10-15	30-35
87695-2	E/20.8% EAR	1.0	10-13	30-35
87695-3	E/13.5% EAR	0.5	20-25	>48
87695-4	E/20.8% EAR	0.5	20-25	>51

¹E is ethylene, EAR is ethyl acrylate, MAR is methyl acrylate.

²DiCup R is dicumyl peroxide

³Knot time is the time required for vulcanization to proceed to a stage where the extrudate begins to develop knots, initial extrudate up to this point is smooth.

⁴Flake time is the time at which vulcanization has gone far enough for the extrudate to be weak, brittle, and infusible.

Comparison of the rheometry data with experimental vulcanization procedures employed to make the previously mentioned films (excessive resistance) indicates the films had been vulcanized to the flake stage or nearly to the flake stage. On the other hand, some films vulcanized to a point just past the knot time were made which had satisfactorily low resistance and were stable in the caustic hydrolyzing medium. These results based on several isolated experiments indicate qualitatively a desirable degree of vulcanization, i.e., into the knot stage but not close to the flake stage. The knot time is significant since vulcanization to this degree insolubilizes the polymer in toluene, while less-vulcanized polymers disintegrate in toluene.

Films have been made by pressing at 150°C because at this temperature polymer may be made that flows satisfactorily and the DiCup R reacts at a suitable speed. Vulcanization for 30 minutes at this temperature effectively utilizes the vulcanizing agent so that additional vulcanization will be nil during future heat treatments. The data of Table 1 indicate that a desirable degree of vulcanization will result under these conditions with about 0.5 wt% DiCup R incorporated in the polymer. Films have been made with this degree of vulcanization which are stable through the hydrolysis process and have low AC resistance. However, the films made with this proportion of vulcanizing agent are not as stable as desired for the sterilization test (60 hours at 140°C in 40% KOH); specifically, the films became crinkled and wadded. Therefore, a slightly greater vulcanization appears desirable. Incorporation of about 0.6 parts DiCup R per 100 parts polymer yields film which appears to be stable during hydrolysis and sterilization and will be used in future preparations.

3.4 Hydrolysis

Vulcanized E/MAR films have been hydrolyzed to E/Acr A films by soaking in caustic. Initially, the films were soaked 7 days at room temperature in 2.5 N alcoholic KOH (1:1 isopropanol:methanol) followed by 7 days at room temperature in 2.5 N aqueous KOH.

A faster hydrolysis method appeared desirable; it was accomplished by increasing the temperature. At about 60-70°C, the vulcanized films were hydrolyzed about 24 hours each in the 2.5 N alcoholic KOH (1:1 isopropanol:methanol) and 2.5 N aqueous KOH.

The methods described above have been satisfactory for small pieces of properly vulcanized film. Large pieces of film tend to get crumpled and stick together. A method has been devised for simultaneous hydrolysis of several pieces of film in a 20-gallon stainless steel kettle.

Alternate layers of film and a porous mesh divider were assembled and placed in the caustic (same solutions used above), which is warmed by a hot plate under the kettle. The multiple-layer structure prevents film from contacting other films and eliminates crumpling. The dividers have been made from a polyethylene mesh with 5/16 in. pores which gives a slightly quilted appearance to the film. A fine pore mesh likely will eliminate the quilt effect.

The hydrolysis procedure outlined here has been successful with film believed to be suitably vulcanized. The relatively high resistance of some film has been attributed to excessive vulcanization which, in turn, may be attributed to incomplete hydrolysis of the highly vulcanized film. If more highly vulcanized film is considered preferable, the hydrolysis process may be modified accordingly. Specifically, hydrolysis at higher temperature (and pressure) may be effective for the highly vulcanized film and may be desirable.

3.5 Polyblending and Carbon Filling

Polyblending and carbon filling are methods of modifying polymers that may improve properties in several ways. Polyblending as used here refers to blending mixtures of widely variable monomer ratios (for E/MAR) and blending E/MAR with different polymers and copolymers. Polyblends are not simple mixtures. Since the mixed polymers are vulcanized together, the polyblends (vulcanized) cannot be extensively separated into individual components without chemical bond rupture.

A polyblend has been made (87716) of 66.7 parts E/21.8 EAR (21.8% ethyl acrylate, 78.2% ethylene) and 33.3 parts of E/67.9 MAR which was vulcanized and hydrolyzed to a membrane comparable (i.e., AC resistance was comparably low) to a membrane made from E/41.3 MAR. However, the polyblend is somewhat less tacky than E/41.3% MAR in the unhydrolyzed state and therefore handles more easily. Another polyblend (82890A) was made by blending E/41.3% MAR with an ethylene/vinyl acetate (E/41.3% VA) copolymer. This polyblend also is easier to handle than the E/MAR alone and the AC resistance is comparably low. These are examples of blends of copolymers which are compatible.

Several blends were made of E/EAR with Hycar 4021 (polyethyl acrylate, from B. F. Goodrich). These blends, surprisingly, gave membranes with high AC resistance, which has been attributed to poor compatibility of the two polymers. Normally, these two might be expected to be compatible, but further examination shows the Hycar 4021 has very high molecular weight (melt index at 190°C of 0.1).

Carbon has been employed as a filler for many thermoplastics and elastomers. Published work indicates that a blend containing up to 50% carbon black is not electrically conductive, but generally is less tacky and often has a greater tensile strength than the polymer without carbon. A polyblend of 3 parts E/31% MAR and 1 part carbon black was mixed on a roll mill, pressed into film, vulcanized, and finally hydrolyzed. Both the hydrolyzed and unhydrolyzed membranes were easy to handle (not tacky) and the AC resistance of the hydrolyzed membranes was low. Preliminary tests indicate that the conductance of the material is a function of the acrylic acid content (but not a function of the carbon), and also that this product may be useful for battery separators.

3.6 Electrical Resistance

AC resistance is an important criteria for battery separators and has been measured here for screening purposes. The membranes are mounted in a Lucite resistance cell on loan from JPL and the resistance measured with an ESI Impedance Bridge, Model 250. The measured resistance of several membranes are shown in Table 2. These membranes were made from E/MAR over a wide range, from E/20% MAR to E/60% MAR. Since the measurements, some of the membranes have been shown to be vulcanized more and some less than appears desirable; more consistent values likely can be obtained.

Experimental data obtained to date allow some conclusions regarding a desirable or optimum monomer ratio in this project. The product from an ethylene copolymer with about 20% methyl acrylate (E/20% MAR) seems to give an E/Acr A product with rather high resistance. The product from E/30% MAR also may have too high a resistance. The product from E/50% MAR and E/60% MAR has a very low resistance. The precursor film, i.e., E/50% MAR and E/60% MAR, is tacky and difficult to handle. From these preliminary considerations, E/40% MAR appears to be a desirable precursor for battery separators.

3.7 Sterilization

The membranes to be made in this project are to be sterilized. Some films have been tested for stability after 60 hours at 140°C in 40% KOH in steel bombs. For these preliminary tests, small samples of film have been used and the AC resistance measured before and after the tests. The results are shown in Table 3.

Table 2

AC RESISTANCE OF E/Acr A MEMBRANES

<u>Sample</u>	<u>Acr A₁</u> <u>%</u>	<u>Membrane</u> <u>Thick₂</u> <u>Mils</u>	<u>R_a</u> <u>ohm-in.²</u>	<u>r</u> <u>ohm-in.</u>	<u>Remarks</u>
82876	16.2	1.5	0.0299	20.0	Under Vulcanized
87684-7	27.1	4.7	0.164	34.9	Over Vulcanized
87684-11	37.1	4.6	0.0866	18.8	Over Vulcanized
82880	37.1	1.0	0.0088	8.84	Under Vulcanized
82979	43.7	5.3	0.055	10.5	
87680-A	55.6	3.8	0.0103	2.71	

¹Remainder of copolymer from ethylene²Films measured wet

Table 3
RESISTANCE OF MEMBRANES BEFORE AND AFTER STERILIZATION¹

Membrane	Composition ²			Film Thick Mils	R _a -ohm-in. ²		r-ohm-in.		Remarks
	E	Acr	A		Before	After	Before	After	
87719-1A	44.3	55.7	0	4.2	0.0069	0.0118	1.56	2.80	Highly Vulcanized
87719-2	56.4	43.6	0	5.7	0.0069	0.0368	1.20	6.45	Under Vulcanized
87719-5	83.8	16.2	0	2.8	0.816	1.29	355	461	Insufficient Acr A
87719-1B	44.3	55.7	0	4.2	0.0108	0.0127	2.25	3.04	Highly Vulcanized
87719-4	83.0	27.0	0	4.6	0.206	0.281	66.5	61.2	Under Vulcanized
87719-6	77.2	22.8	0	6.0	2.21	1.39	522	252	Insufficient Acr A
87735-A	60.8	31.8	0 ³	5.1	0.0491	0.234	10.09	45.9	Insufficient Acr A
87735-B	46.4	27.3	26.3	3.9	0.0090	0.0451	1.75	11.6	

¹160 hours, 140°C, in 40% KOH

²All films vulcanized and hydrolyzed. Composition exclusive of DiCup R residue and Armid O, a release agent. E=ethylene, Acr A=acrylic acid, C=statex R (carbon black from Columbian Chemical Company).

³Also contains ca 7.5% vinyl alcohol resulting from incorporation of E/41.3% VA in polyblend.

The specific resistance (r) of many of these films after sterilization is less than 20 ohm-in., and most of the membranes are in excellent condition. The under-vulcanized samples were crinkled and seemed to be in undesirable condition, even though they were good enough for the measurement. In most examples, the resistance increased somewhat with sterilization; this increase may be a function of the degree of vulcanization. The lowest resistances were obtained with the high acrylic acid copolymers which also seem to be least sensitive to degree of vulcanization.

4. LIAISON

The project monitor, Mr. Werner von Hartmann, visited the laboratory on 29 February 1968. Project progress was briefly described, and an alternate approach to battery separators not covered in this project and some other items of interest were discussed.

E/MAR film, 1 mil thick, has been shown to be difficult to prepare in a hot press and somewhat thicker film was agreed will be applicable in batteries, as well as easier to prepare in a hot press. Therefore, the sizable product of this project (100 feet of film) will be thicker than 1 mil and thinner than 5 mil and will be made in a hot press. If desirable at a later date, we are confident a process for making 1 mil film can also be developed by blow extruding or by solution casting.

5. FUTURE PLANS

Membranes of E/Acr A will be made from several specified E/MAR copolymers for measurement of resistance and sterilization stability for the purpose of recommending a desirable product for battery separators.

With approval of JPL on choice of copolymer, production of 100 feet of acceptable film (1-5 mil) will be started in a 20 in. x 20 in. hot press (French Oil Machine Company, 100 ton ram force) which is being readied for the work.

As time permits, some carbon-filled membranes will be prepared and evaluated.